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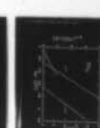
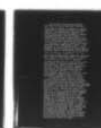
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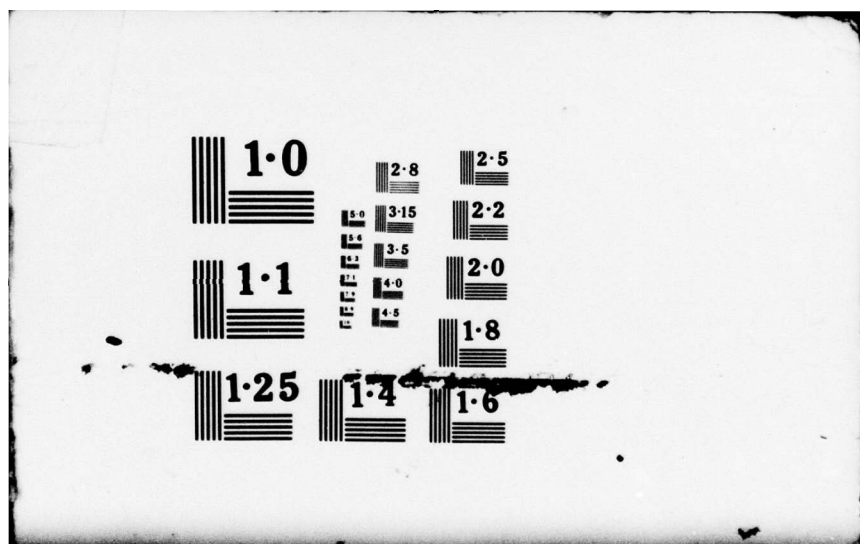
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Measurements of the quantum efficiency of the photoelectrolysis of water, using semiconducting oxide anodes of high conductivity ($\sim 1 \Omega \text{cm}$), are used to determine the energies of the interband transitions of the oxides. The previously determined values for the band gaps of TiO_2 and SrTiO_3 are confirmed, and new values are reported for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (3.28 eV indirect, (cont on reverse side))

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3.92 and 4.19 eV direct), WO_3 (2.62 eV indirect,
3.52 and 3.74 eV direct) and Fe_2O_3 (1.88 eV indirect,
2.75 eV direct).

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TECHNICAL REPORT NO. 5

INTERBAND TRANSITIONS OF SEMICONDUCTING OXIDES DETERMINED FROM PHOTOELECTROLYSIS SPECTRA

F. P. Koffyberg, K. Dwight, and A. Wold*

Department of Chemistry, Brown University
Providence, Rhode Island 02912

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INTERBAND TRANSITIONS OF SEMICONDUCTING OXIDES DETERMINED FROM PHOTOELECTROLYSIS SPECTRA

F. P. Koffyberg*, K. Dwight, and A. Wold

Department of Chemistry, Brown University
Providence, Rhode Island 02912

(Received 9 March 1979 by J. Tauc)

Measurements of the quantum efficiency of the photoelectrolysis of water, using semiconducting oxide anodes of high conductivity ($\approx 1 \Omega\text{cm}$), are used to determine the energies of the interband transitions of the oxides. The previously determined values for the band gaps of TiO_2 and SrTiO_3 are confirmed, and new values are reported for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (3.28 eV indirect, 3.92 and 4.19 eV direct), WO_3 (2.62 eV indirect, 3.52 and 3.74 eV direct) and for Fe_2O_3 (1.88 eV indirect, 2.75 eV direct).

The electrolytic decomposition of water using photosensitive semiconducting electrodes has been the subject of intensive research recently.^{1,2} In this process an n-type semiconducting oxide functions as the anode, which is suitably biased to form a depletion layer at its surface. Electron hole pairs, generated upon illumination with photons of $h\nu > E_g$, are separated in the field of the depletion layer, and the holes react at the surface with OH^- ions from the solution to form oxygen. The electrons are transferred via an external circuit to the cathode, where they react with the H^+ ions to form hydrogen. The overall quantum efficiency η of the process is determined both by the optical and electronic properties of the semiconductor, as well as by the actual electrochemical reactions at the surfaces. In this report we will show that, under suitable conditions, the wavelength dependence of η can give reliable information about the interband transitions of the semiconductor at photon energies much larger than the lowest band gap.

It has been shown³ that, under moderate illumination, the overall reaction rate is not limited by the electrochemical hole and electron transfers at the surfaces to the solution, but by the arrival rate of holes at the anode surface. Now the hole current in the semiconductor is the sum of two components: One due to holes generated in the depletion layer, and the other due to holes generated in the bulk which must diffuse to the depletion layer. The quantum efficiency is then given by³:

$$\eta = 1 - [\exp(-\alpha W)] / (1 + \alpha L_p)$$

where α is the optical absorption coefficient, L_p is the hole diffusion length and W is the width of the depletion layer. $W = [2\epsilon\epsilon_0(V - V_b)/eN_0]^{1/2}$ when ϵ is the dielectric constant, N_0 is the donor concentration and $(V - V_b)$ is the band bending due to the applied bias. Therefore, η is proportional to α if both $\alpha W < 1$ and $\alpha L_p < 1$.

Since $\alpha \sim (h\nu - E_g)^n / h\nu$, then the intercept of plots of $(\eta h\nu)^{1/n}$ versus $h\nu$ should give the energies of the band gaps; $n = 2$ for indirect allowed transitions, $n = 1/2$ for direct allowed transitions and $n = 3/2$ for direct forbidden transitions.

For the group of materials considered here both W and L_p are less than $\approx 10^{-6}$ cm, which makes it possible to determine interband transitions at energies well above the lowest band gap. With the possible exception of SrTiO_3 , these oxides are low mobility, hopping-type semiconductors, which can be made conducting by reducing an appreciable fraction of the transition metal ions to a lower valence state. For example, for our SrTiO_3 sample: $\rho = 0.014 \text{ } \Omega\text{cm}$, $\mu = 6 \text{ cm}^2/\text{Vs}$ and $N_0 = 7.5 \times 10^{19} \text{ cm}^{-3}$ (from Hall effect measurements); with $\epsilon = 330$ we obtain $W = 2 \times 10^{-6} \text{ cm}$ for $(V-V_b) = 1 \text{ Volt}$. Moreover, for these highly defect oxides the hole diffusion length is determined by bulk recombination,³ so that $L_p \leq (\epsilon \epsilon_0 kT / e^2 N_0)^{1/2} \approx 10^{-7} \text{ cm}$.

Most other transition metal oxides have mobilities of $0.1 \text{ cm}^2/\text{Vs}$ or less; then with $\rho \approx 1 \text{ } \Omega\text{cm}$ we still obtain $L_p < W \approx 10^{-6} \text{ cm}$. Therefore,

in these materials the only contribution to the hole current is from pairs generated in the depletion layer. Then η will be proportional to α for $\alpha \leq 10^6 \text{ cm}^{-1}$, thus permitting the determination of interband transitions well above the lowest band gap. It should be noted, however, that the small values of L and W correspond to quantum efficiencies much smaller than desirable in practical devices.

The validity of this approach has been tested on TiO_2 and SrTiO_3 ; for both materials band structure calculations have been made^{5,6,7} and experimental data are available for comparison. Measurements were made under conditions previously⁸ described; the electrolyte was 0.2 M sodium acetate solution. The cell was biased in the range $0.4 < (V-V_b) < 1.8 \text{ Volt}$; band gap energies were found to be independent of bias. Samples were cut from commercial boules,⁹ the TiO_2 samples was sliced parallel to the c -axis. Samples ($\approx 0.1 \text{ cm}$ thick) were made conducting by reduction in hydrogen for 8 hrs at 700°C for TiO_2 and at 850°C for SrTiO_3 ; the resulting resistivities are listed in Table I. η was determined by dividing the current through the cell by the incident photon flux, measured with a calibrated Si photodiode. At the longest wavelengths the accuracy is limited by the very small photocurrents; therefore the energy of the lowest band gap is the least accurate. The values listed in Table I are the averages obtained from a number of samples.

Fig 2

TABLE I
Interband Transition Energies

	ρ (Ωcm)	Band Gap Energies (eV)
TiO_2	0.19	3.02(i); 3.24(i); 3.65(d)
SrTiO_3	0.014	3.21(i); ~3.4; 3.78(d)
$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$	0.88	3.28(i); 3.92(d); 4.19(d)
WO_3	0.75	2.62(i); 3.52(d); 3.74(d)
Fe_2O_3	1.12	1.88(i); 2.75(d)

(i): indirect; (d): direct

For TiO_2 our results (Fig. 1) show that the first two transitions are indirect ($n=2$) at 3.02 ± 0.05 and 3.24 ± 0.02 eV; these values are in good agreement with the gaps (3.02 and 3.3 eV) from electromodulation spectra.^{10,11} The next transition at 3.65 ± 0.05 eV is direct ($n=1/2$). The values predicted from the band structure calculation⁵ are 3.05, 3.19 and 3.59 eV, for a polarization $E//c$; within experimental error our values are independent of polarization, indicating that the dichroism is less than 50 meV.

The lowest bandgap of SrTiO_3 (Fig. 2) is indirect, at 3.21 ± 0.03 eV, in good agreement with the results from absorption measurements¹² (3.22 eV) and the calculation of Kahn and Leyendecker⁶ (3.15 eV). Our data show increased absorption for $h\nu > 3.4$ eV; however, no well defined transition energy could be determined in this range, even after subtracting the extrapolated absorption from the 3.21 eV gap. Electromodulation spectra¹³ also show increased absorption in this region, without a well defined critical point. The first direct transition is at 3.78 ± 0.04 eV; the electromodulation measurements¹³ place it at 3.81 eV, whereas the band structure calculation⁶ predicts 3.75 eV.

Fig 3

Since from the preceeding it is clear that band gaps can be determined reliably from photoelectrolysis spectra, we applied the technique to other transition metal oxides with the following results: The lowest band gap of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ is indirect, at 3.28 ± 0.03 eV, (Fig. 3) followed by two direct gaps at 3.92 ± 0.02 and 4.19 ± 0.04 eV (Fig. 4). The absorption tail below 3.3 eV was not reproducible between different samples, and may represent transitions to surface states or to defect states just below the band gap. The samples used were sintered polycrystalline discs, reduced in hydrogen at 700°C for 8 hrs.

In WO_3 the lowest band gap is indirect at 2.62 ± 0.04 eV, in fair agreement with a previous determination.³ At higher energies two distinct direct gaps are found at 3.53 ± 0.02 and 3.74 ± 0.03 eV. The measurements were made on a sintered polycrystalline disc prepared by reacting weighed amounts of WO_3 and tungsten metal in an evacuated sealed tube for 24 hrs at 800°C to form $\text{WO}_{2.95}$, followed by a similar reaction of this $\text{WO}_{2.95}$ with WO_3 to form $\text{WO}_{2.995}$.

Fig. 4

In Fe_2O_3 the lowest band gap is again indirect at 1.88 ± 0.04 eV in good agreement with previous data.¹⁴ The first direct transition is at 2.75 ± 0.03 eV. The measurements were made on a single crystal grown by chemical vapor transport using tellurium tetrachloride with a small amount of titanium tetrachloride to provide conductivity via Ti doping.

In conclusion, the quantum efficiency of the photoelectrolysis of water on conducting oxide anodes is directly proportional to the absorption coefficient of the oxide if both the depletion layer width and the hole recombination length are smaller than the light penetration depth. Under these conditions one can determine the energies of the interband transitions of the oxides from the photoelectrolysis spectra.

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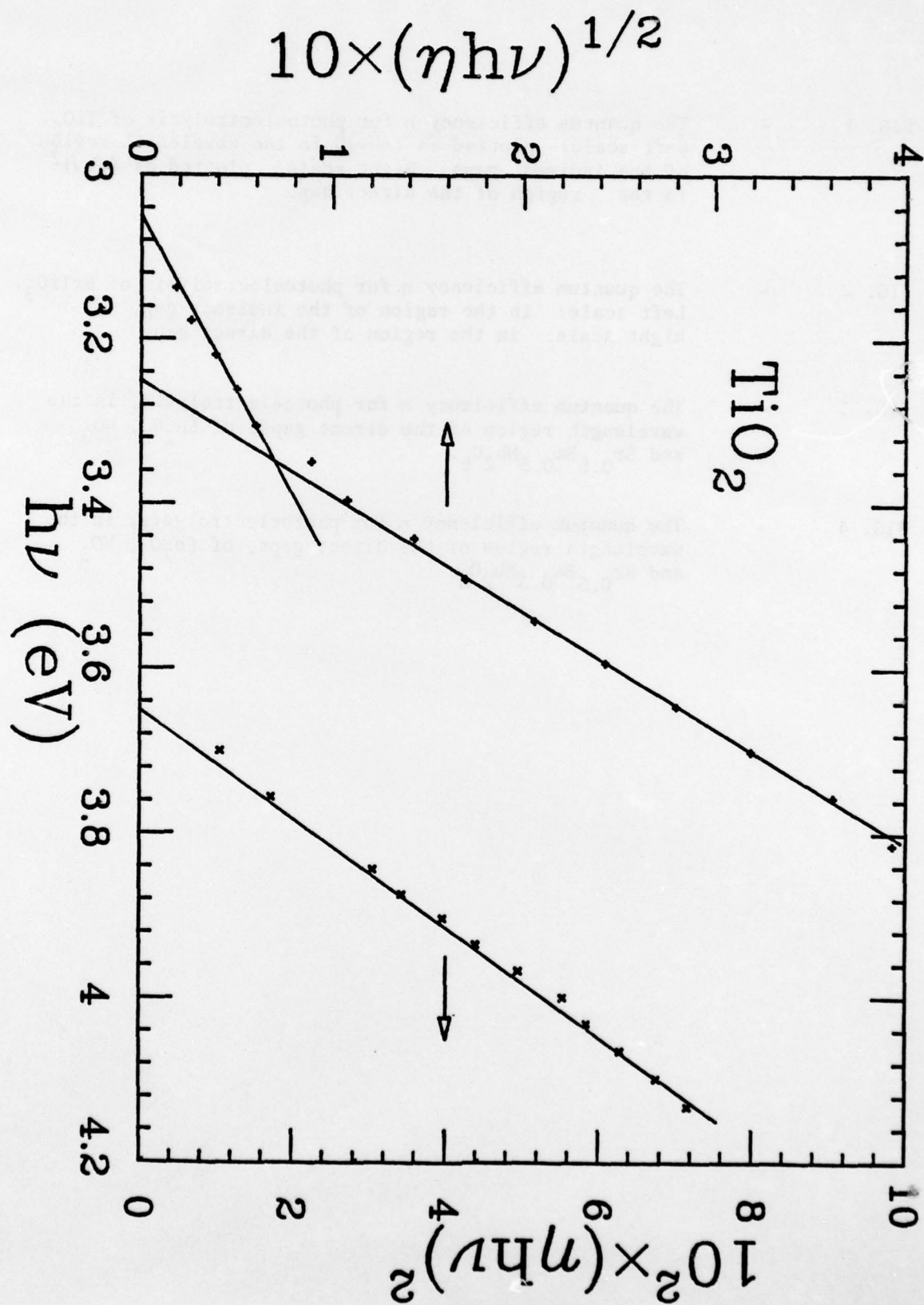
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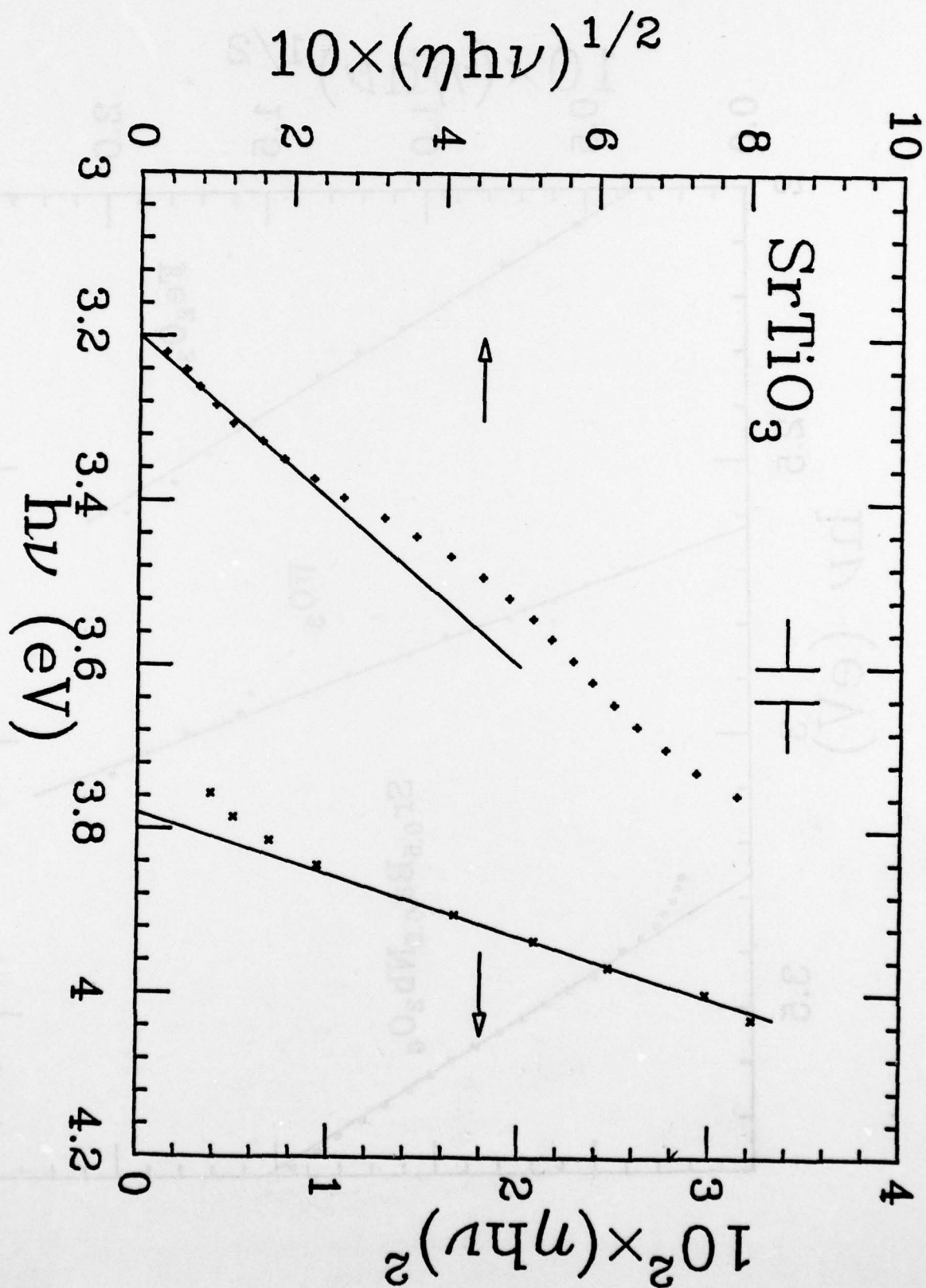
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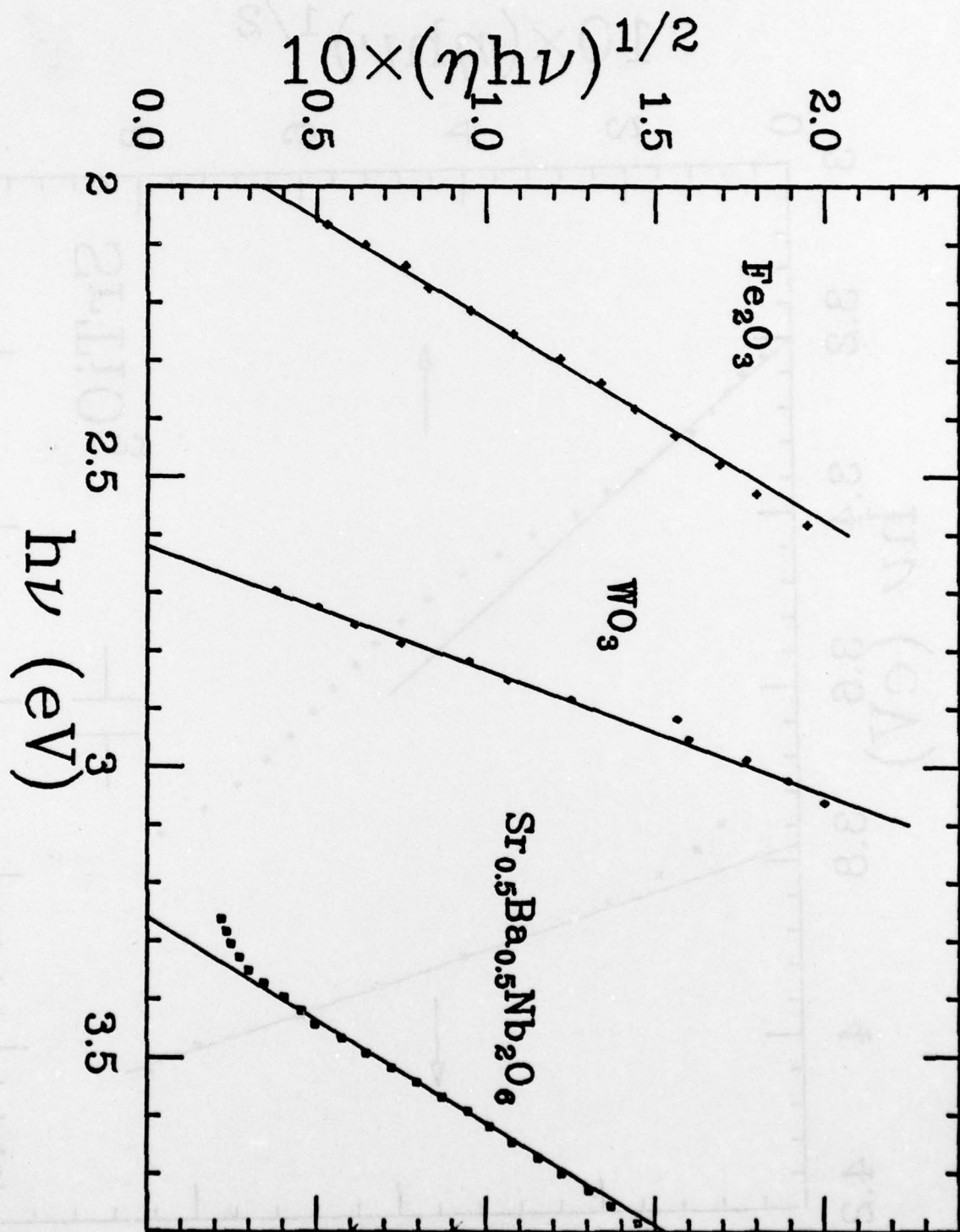
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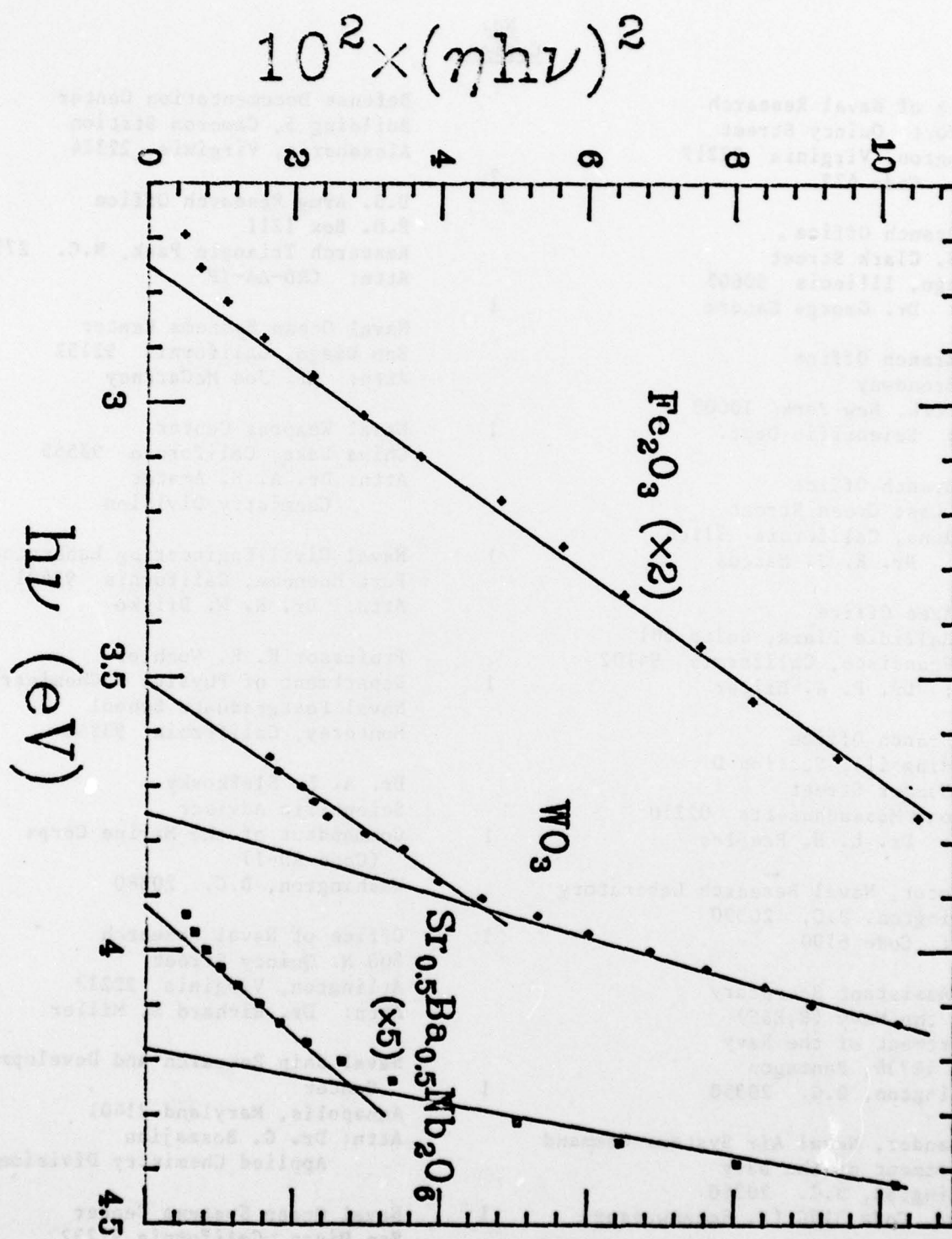
FIGURE CAPTIONS

- FIG. 1 - The quantum efficiency η for photoelectrolysis of TiO_2 . Left scale: plotted as $(\eta h\nu)^{1/2}$ in the wavelength region of the indirect gaps. Right scale: plotted as $(\eta h\nu)^2$ in the region of the direct gap.
- FIG. 2 - The quantum efficiency η for photoelectrolysis of SrTiO_3 . Left scale: in the region of the indirect gap. Right scale: in the region of the direct gap.
- FIG. 3 - The quantum efficiency η for photoelectrolysis, in the wavelength region of the direct gaps, of Fe_2O_3 , WO_3 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$.
- FIG. 4 - The quantum efficiency η for photoelectrolysis, in the wavelength region of the direct gaps, of Fe_2O_3 , WO_3 and $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$.









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